

The ground state phases of orbitally degenerate spinel oxides

George Jackeli *

*Institute for Theoretical Physics, Ecole Polytechnique Fédérale de Lausanne, CH-1025, Lausanne, Switzerland,
and E. Andronikashvili Institute of Physics, Tbilisi, Georgia.*

Abstract

I review the microscopic spin-orbital Hamiltonian and ground state properties of spin one-half spinel oxides with threefold t_{2g} orbital degeneracy. It is shown that for any orbital configuration a ground state of corresponding spin only Hamiltonian is infinitely degenerate in the classical limit. The extensive classical degeneracy is lifted by the quantum nature of the spins, an effect similar to order-out-of-disorder phenomenon by quantum fluctuations. This drives the system to a non-magnetic spin-singlet dimer manifold with a residual degeneracy due to relative orientation of dimers. The magneto-elastic mechanism of lifting the “orientational” degeneracy is also briefly reviewed.

Key words: Spin-Orbital models, spinel oxides, geometrical frustration

PACS: 75.10.Jm, 75.30.Et

1. Introduction

The pyrochlore lattice which is composed by corner sharing tetrahedra, is known to be the most frustrated lattice existing in the nature. For the Heisenberg antiferromagnet on pyrochlore lattice the order-out-of-disorder mechanisms are inactive [1] and such a spin system would remain liquid down to the lowest temperatures [2].

However, in real compounds magnetic ions, forming a frustrated lattice, often possess an orbital degeneracy in addition to the spin one. In such cases, orbital degrees of freedom are also incorporated in the superexchange theory and the systems are described by means of an effective Kugel-Khomskii type spin-orbital model [3]. The exchange interaction between magnetic moments on a bond depends now on the orientation of occupied electronic orbitals with respect to that bond. The physical behavior of such systems is expected to be drastically

different from that of pure spin models, as the occurrence of an orbital ordering can modulate the spin exchange and partially or fully release the geometrical degeneracy of the underlying lattice.

The compounds that we have in mind are transition metal (TM) spinels. The systems which are the subject of intense experimental and theoretical activity [4]. All spinels have the general formula AB_2O_4 and here we will be dealing with situation when B sites with octahedral coordination are occupied by magnetic TM ions with orbital degeneracy. The most interesting feature of the spinel structure is the fact that the B ions form a highly frustrated pyrochlore lattice [See Fig.1]. These systems thus give the unique possibility to explore how the natural tendency of correlated systems to develop magnetic and orbital is effected by geometrical frustration.

The degeneracy of the d -shell of TM ions is not fully lifted by the ligand field with octahedral symmetry and local electronic structure is composed by high energy e_g doublet and low energy t_{2g} triplet. In the case of partial filling of the t_{2g} manifold,

* Tel: +41 21 693 44 79; fax: +41 21 693 54 19.

E-mail address: george.jackeli@epfl.ch

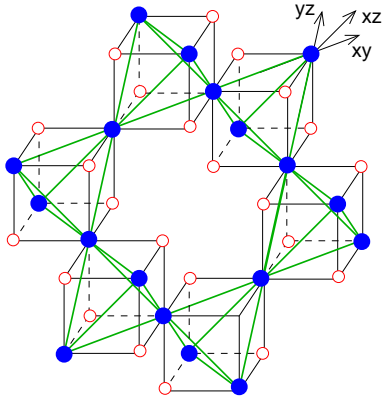


Fig. 1. The pyrochlore lattice formed by B sites in the spinel structure AB_2O_4 : only B (colored circles) and O (white circles) sites are shown.

(d_{xy} , d_{xz} , and d_{yz} orbitals), one encounters with the threefold orbital degeneracy in d^1 and d^2 systems. The first case corresponds to Ti^{3+} spinels, such as $MgTi_2O_4$ [5,6], and the second case to V^{3+} spinels AV_2O_4 , where $A=Zn, Mg, Cd$ [7,8]. Although both cases are described by similar Hamiltonians the physics of $S = 1/2$ and $S = 1$ systems are drastically different. In what follows, I focus on the spin one-half d^1 system and refer the readers to Refs.[9,10,11] for the discussion of d^2 systems.

The theoretical studies of the effective model for titanium spinels have been performed in Refs. [12,13]. Here, I briefly review the obtained results, however, within a different and complimentary scheme of reasoning.

2. Effective spin-orbital Hamiltonian

We assume that the low-temperature insulating phase of $MgTi_2O_4$ is of Mott-Hubbard type. However, the alternative description of the insulating phase starting from the band picture is also possible and is given in Ref. [14].

In the Mott phase, an effective low energy spin-orbital Hamiltonian can be derived with the standard second-order superexchange theory and has been reported in Refs.[12,13]. The peculiarity of the spinel structure is due to the fact that electron transfer between the nearest-neighbor (NN) sites of B-sublattice is governed by the direct $dd\sigma$ overlap of t_{2g} orbitals. The $dd\sigma$ overlap in $\alpha\beta$ plane connects only the corresponding orbitals of the same $\alpha\beta$ type. The pyrochlore lattice, formed by B-ions, can also be viewed as a collection of crossing chains running in xy , yz , and xz directions, as seen in Fig. 1. Along the

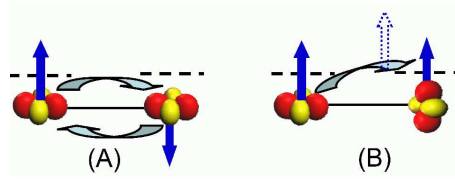


Fig. 2. Orbital arrangements on (A) antiferromagnetic and (B) ferromagnetic bonds.

bond, for example in xy direction, only the diagonal overlap between xy orbitals are nonzero. Therefore the total number of electrons in each orbital state at a given site is a conserved quantity and the orbital part of the effective Hamiltonian H has no dynamics. The orbital degrees are thus Potts-like Z_3 static variables. The spin-orbital Hamiltonian has the following form:

$$H = 4J_{AF} \sum_{\langle ij \rangle} [\vec{S}_i \cdot \vec{S}_j - \frac{1}{4}] O_{ij}^{OF} - \sum_{\langle ij \rangle} [J_O + J_F \vec{S}_i \cdot \vec{S}_j] O_{ij}^{OAF} \quad (1)$$

where the sum is over pairs of nearest-neighbor sites of the pyrochlore lattice. The first term describes antiferromagnetic coupling between the NN spins and is active when the bond is occupied by the corresponding orbitals of the same type [see Fig.2A]. For the bond ij in $\alpha\beta$ -plane we have $O_{ij}^{OF} = P_{i,\alpha\beta} P_{j,\alpha\beta}$, where $P_{i,\alpha\beta}$ is a projector operator and is equal to 1 when $\alpha\beta$ orbital on site i is occupied and is zero otherwise. When the bond ij in $\alpha\beta$ -plane is occupied by two different orbitals, one of them being of $\alpha\beta$ type [see Fig.2B], then there is gain of energy J_O , independent of spin configuration on the bond. This is given by the second term of the Hamiltonian. However, in the same situation, the local Hund's coupling J_H favors the parallel orientation of the spins and introduces a weak ferromagnetic (FM) coupling J_F between them, described by the last term in the Hamiltonian. Along the bond in $\alpha\beta$ -plane $O_{ij}^{OAF} = P_{i,\alpha\beta}(1 - P_{j,\alpha\beta}) + P_{j,\alpha\beta}(1 - P_{i,\alpha\beta})$. There is a local constraint $P_{i,xy} + P_{i,xz} + P_{i,yz} = 1$ as we have one electron at each site. The coupling constants can be expressed in terms of $J = t^2/U$, defining the energy scale of the problem, and parameter $\eta = J_H/U$ measuring the strength of the Hund's coupling with respect of local Coulomb repulsion U . For TM ion $\eta = J_H/U \ll 1$ and is of the order of 0.1. In this limit we have $J_{AF} \simeq J_O \sim J$, and $J_F \sim \eta J$ [12,13].

3. The ground state phases

We start our analysis of the ground properties from well defined realistic limit $\eta = 0$. In this case the Hamiltonian Eq.(1) simplifies and takes the following form:

$$\mathcal{H} = E_S + 4J \sum_{\langle ij \rangle} [\vec{S}_i \cdot \vec{S}_j + \frac{1}{4}] O_{ij}^{\text{OF}} \quad (2)$$

where $E_S = -2JN$ is the constant energy shift due to spin uncorrelated virtual fluctuations and N is the number of sites. In deriving Eq.(2) we have used the fact that each lattice site has nearest-neighbors in all three directions xy , xz , and yz , and the constraint for projection operators given above.

The first observation is, that in the limit $\eta = 0$ the only bonds occupied with corresponding same type orbitals give the contribution to the energy. The spin exchanges on such bonds are antiferromagnetic. Different orbital configurations will have different number and pattern of AFM exchange of underlining spin subsystems, and, in principle, different ground state energy. However, for classical Neel type configuration of spins on such bonds $\langle \vec{S}_i \cdot \vec{S}_j \rangle = -1/4$ and the second term in Eq.(2) vanishes. It thus follows that for any orbital pattern the spin subsystem have the same classical energy and the classical ground state is infinitely degenerate.

As we have noted above each occupied orbital has finite overlap only along corresponding chain. It is easily verified that interacting AFM bonds can only be connected along the straight lines. Therefore, for each orbital configuration, the spin-subsystem can be viewed as a collection of decoupled finite (or infinite) antiferromagnetic spin one-half chains. The deviation from classical value $\langle \vec{S}_i \cdot \vec{S}_j \rangle = -1/4$ on AFM bond can be significant for spin one-half one dimensional objects. For antiferromagnetically coupled quantum spins the ground state expectation value $\langle \vec{S}_i \cdot \vec{S}_j \rangle$ is always smaller than $-1/4$ and in this case we have finite energy gain due the second term of the Hamiltonian Eq. (2). The quantum energy per bond depends on the length of such spin chains. With increasing the size of AFM chain we have more bonds to gain the energy, however the amount of energy we gain decreases. The maximum energy gain per bond is for the cluster of two spins coupled into singlet state, for which we have $\langle \vec{S}_i \cdot \vec{S}_j \rangle = -3/4$. It then appears that the minimum energy configuration corresponds to such an orbital pattern for which isolated non-interacting spin-singlet dimers

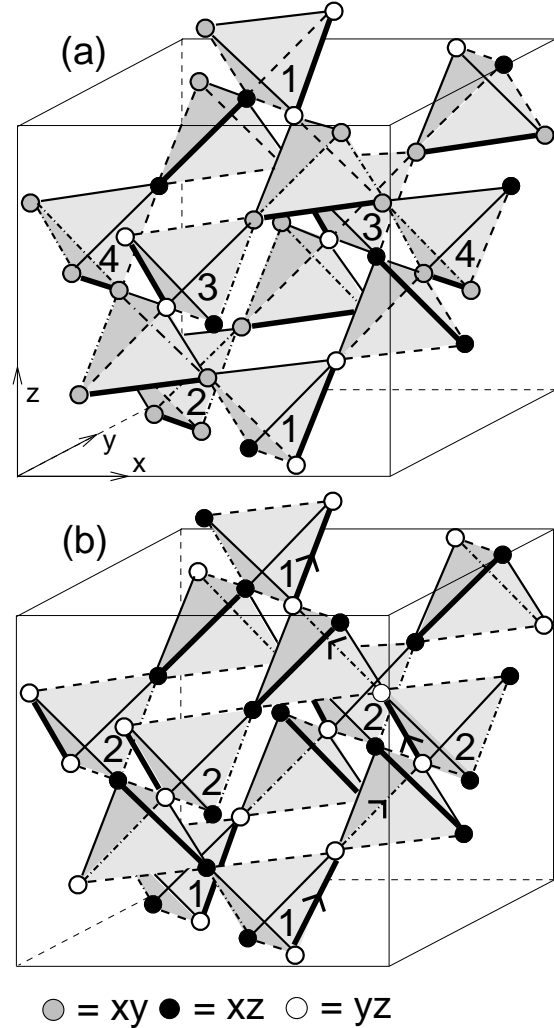


Fig. 3. Two different coverings of the unit cubic cell through dimers. Locations of singlets are represented by thick links. Different numbers correspond to inequivalent tetrahedra.

are formed [12,15]. The quantum nature of spins removes the spin degeneracy and drives the system to spin-singlet nonmagnetic dimer manifold. However, the latter is highly degenerate with respect of dimer orientations. One of the possible dimer coverings of the lattice is shown in Fig. 3a. The dimers in the limit $\eta = 0$ are noninteracting and the effective dimensionality of the systems is zero. In the present case, as in a spin-Peierls system, the increase of magnetic energy gain due to the shortening of strong bonds outweighs the increase in elastic energy due to the distortion of lattice. Therefore, each type of dimer covering induces corresponding distortion of the lattice and different distortion pattern will cost different elastic energy. Therefore, the “orientational” de-

generacy of dimer phase can be lifted by the elastic energy cost. We have shown in Ref.[12,13] that magneto-elastic interaction indeed lifts the “orientational” degeneracy and stabilizes the dimer pattern leading to the minimal enlargement of the unit cell. This generates a condensate of dimers in a valence bond crystal state, forming one dimensional dimerized helical chains, indicated by arrows in Fig. 3b, running around the tetragonal c -axis. Such a dimerized pattern has been actually observed in MgTi_2O_4 [6]. There is a peculiar orbital ordering in the dimerized phase: a ferro-type order along the helices with antiferro-type order between them (see Fig. 3b).

Finally, let us briefly comment on the effect of finite Hund’s coupling $\eta \neq 0$. The latter induces the ferromagnetic coupling, $J_F \simeq \eta J$, between the spins belonging to different dimers. For FM coupling much smaller than the binding energy of the spins into spin-singlet state $J_{FM} \ll \Delta \simeq 4J$, the dimer state is stable against weak interdimer coupling. With increasing η one finds only one phase transition, presumably first order, from singlet-state to a ferromagnetic state with a different orbital ordering [12,13]. The dimer state and ferromagnetic spin order are only possible ground state phases of spin-orbital Hamiltonian Eq.(1).

Acknowledgements I am very grateful to S. Di Matteo, C. Lacroix, and N. Perkins for their collaborations and numerous discussions on this topic. The support by GNSF under the Grant No.06-81-4-100 is acknowledged.

References

- [1] R. Moessner and J. T. Chalker, Phys. Rev. Lett. **80**, 2929 (1998);
- [2] B. Canals and C. Lacroix, Phys. Rev. Lett. **80**, 2933 (1998).
- [3] K. I. Kugel and D. I. Khomskii, Usp. Fiz. Nauk **136**, 621 (1982) [Sov. Phys. Usp. **231**, 25 (1982)].
- [4] For a recent review see P.G. Radaelli, New Journal of Physics **73**, 53 (2005).
- [5] M. Isobe and Y. Ueda, J. Phys. Soc. Jpn. **71**, 1848 (2002).
- [6] M. Schmidt *et al.*, S. W. Cheong, Phys. Rev. Lett. **92**, 056402 (2004).
- [7] M. Reehuis *et al.*, Eur. Phys. J. B **35**, 311 (2003).
- [8] S.-H. Lee *et al.*, Phys. Rev. Lett. **93**, 156407 (2004).
- [9] H. Tsunetsugu and Y. Motome, Phys. Rev. B **68**, 060405(R) (2003); Y. Motome and H. Tsunetsugu, *ibid.* **70**, 184427 (2004).
- [10] O. Tchernyshyov, Phys. Rev. Lett. **93**, 157206 (2004).
- [11] S. Di Matteo, G. Jackeli, and N. B. Perkins, Phys. Rev. B **72**, 020408(R) (2005).
- [12] S. Di Matteo, G. Jackeli, C. Lacroix, and N. B. Perkins, Phys. Rev. Lett. **93**, 077208 (2004).
- [13] S. Di Matteo, G. Jackeli, and N. B. Perkins, Phys. Rev. B **72**, 024431 (2005).
- [14] D. I. Khomskii and T. Mizokawa, Phys. Rev. Lett. **94**, 156402 (2005).
- [15] The rigorous proof will be given elsewhere.